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Dimethylsulfide (DMS) in the equatorial Pacific Ocean (1982 to 1996): Evidence of a climate feedback?

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Abstract. Oceanic dimethylsulfide (DMS) is the major natural source of sulfur to the atmosphere. The equatorial Pacific Ocean is a region of relatively high DMS emissions that persist throughout the year. Measurements from 11 cruises between 1982 and 1996 show that the mean surface seawater DMS concentration in this region (15°N to 15°S) is relatively constant both seasonally and interannually (2.7 ± 0.7 nM). The large interannual variations in oceanic and atmospheric properties associated with El Niño-Southern Oscillation (ENSO) events appear to have little effect on the concentration of DMS in surface ocean waters.

Introduction

Emissions of DMS from the equatorial Pacific Ocean are a significant source of sulfur to the atmosphere and contribute both to the tropospheric sulfur burden and to particle growth in the marine boundary layer. The atmospheric sulfate aerosol particles that evolve from biogenically derived DMS emissions play a role in the global radiation balance directly through the upward scatter of solar radiation and indirectly as cloud condensation nuclei (CCN). Evidence for the climatic significance of DMS emissions continues to grow, linking regions (periods) of high DMS emissions with regions (periods) of high particle concentration and enhanced cloud albedo. However, the hypothesized feedback link whereby climate affects the level of DMS emissions [*Charlson et al.*, 1987] has remained elusive.

The equatorial Pacific Ocean is an ideal natural environment to assess DMS-climate feedbacks. The region is characterized by a westward flowing south-equatorial current (SEC), large-scale upwelling of nutrient-rich water along the equator, and a highly productive phytoplankton community. Periodically this characteristic pattern is disturbed by an El Niño-Southern Oscillation (ENSO) event which results in higher sea-surface temperatures (SST), lower nutrient concentrations, lower primary productivity rates, lower chlorophyll biomass concentrations, changes in phytoplankton speciation, and increases in rainfall [reviewed by *Murray et al.*, 1992]. The large interannual variations in oceanic (SST, mixed layer depths, and upwelling rates) and atmospheric (cloud cover and precipitation) properties associated with ENSO events provide a natural laboratory in which to search for a feedback between DMS emissions and environmental variables. This region is especially interesting in light of the results from a recent iron fertilization experiment in the eastern equatorial Pacific Ocean which showed a factor of 3.5 increase in DMS concentration in iron-enriched waters [*Turner et al.*, 1996]. What remains to be seen is how the interannual variability associated with ENSO affects seawater concentrations of DMS.

Seawater DMS measurements have been made by PMEL in the equatorial Pacific Ocean since 1982 [*Cline and Bates*, 1993; *Bates et al.*, 1987, 1992b, 1993; *Kiene and Bates*, 1990; *Quinn et al.*, 1990; *Huebert et al.*, 1994; *Kieber et al.*, 1996; *Yvon et al.*, 1996). The PMEL equatorial DMS database, which includes over 4300 measurements from 11 research cruises (Figure 1, Table 1), spans 15 years and provides an opportunity to assess interannual variations in seawater DMS concentrations that may be related to a DMS–climate feedback.

Methods

Seawater DMS measurements were made from 1982–1989 with a manually operated purge-and-trap system and a gas chromatograph with a flame photometric detector (FPD) [*Quinn et al.*, 1990]. In 1990, seawater DMS concentrations were calculated from seawater-equilibrated air samples measured with an electron capture detector (ECD)-sulfur system [*Bates et al.*, 1993]. In 1992 the seawater purge-and-trap system was automated. The automated system was operated in 1992 and 1993 with an FPD [*Yvon et al.*, 1996] and in 1994 through 1996 with a sulfur chemiluminesence detector (SCD). All systems were calibrated with periodic injections of a standard volume of DMS in air which was generated from gravimetrically calibrated permeation tubes. The precision of the method, based on replicate analyses of a single water sample, typically was ±8%.

The DMS system has been intercalibrated in the field with the NOAA Aeronomy Laboratory [*Bates et al.*, 1990], the Rosenstiel School of Marine and Atmospheric Science (RSMAS) [*Bates et al.*, 1994; *Yvon et al.*, 1996], the University of Georgia [*Kiene and Bates*, 1990], and the State University of New York [*Kieber et al.*, 1996]. In all cases, the comparisons were within the precision of the analysis.

Surface seawater nitrate measurements were made with an automated autoanalyzer technique which ran an hourly cycle of standard, blank, seawater, blank, seawater, blank. The detection limit was generally 0.05 μM but at times was as low as 0.01 μM. Surface seawater nitrate concentrations of 2.5 μM, measured at the equator on the MAGE 1992 cruise, are consistent with the values reported by *Murray et al.* [1995] for the same location and time period.

Results and Discussion

The equatorial Pacific Ocean, as defined by seawater DMS concentrations, stretches from 15°N to 15°S. Although there is considerable variation in DMS concentrations with latitude within this region, concentrations poleward of 15° are lower (Figure 2) and more typical of those found in the oligotropic central gyres of the ocean [*Bates et al.*, 1987]. The mean annual DMS concentration in the region from 5°N to 15°S, correspond-

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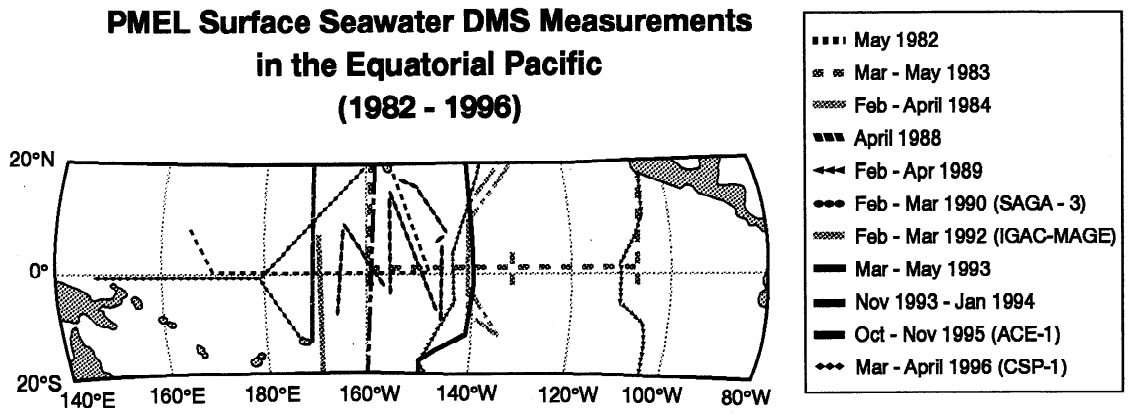

Figure 1. PMEL equatorial DMS cruise tracks from 1982–1996.

ing to the SEC, is 3.2 ± 0.7 nM. The southern boundary (approximately 15°S) reflects the end of the zone of enhanced chlorophyll (>0.1 mg/m^3) relative to the oligotrophic ocean. The northern boundary (approximately 5°N) is the Equatorial Front, which separates the tropical surface waters of the North Equatorial Counter Current (NECC) and the recently upwelled waters of the SEC. This boundary can undulate several degrees north and south as tropical instability waves (TIW) propagate across the Pacific with periods of 20–30 days. These TIW create significant temperature, salinity, and nutrient gradients within the SEC [*Feely et al.*, 1994] and may be responsible for some of the sharp DMS concentration gradients observed within this region (Figure 2). The region from 5°N to 15°N is somewhat of a transition zone and reflects the seasonal migration of the Intertropical Convergence Zone (ITCZ) and the Equatorial Front. The mean annual DMS concentration in this region is 2.0 ± 0.7 nM.

Table 1. PMEL Surface Seawater DMS Measurements in the Equatorial Pacific (1982–1996)

Cruise	Date	Location
PMEL-1982	4 May 1982	Honolulu, HI
(*Discoverer*)	12 May 1982	0°N, 148°W
	21 May 1982	Kwajalein, Marshall Is.
PMEL-1983	2 April 1983	Honolulu, HI
(*Discoverer*)	8 April 1983	0°N, 158°W
	28 April 1983	0°N, 105°W
	2 May 1983	Manzanillo, Mexico
PMEL-1984	12 April 1984	20°S, 170°W
(*Discoverer*)	28 April 1984	11°N, 170°W
RITS-1988	6 April 1988	Dutch Harbor, AK
(*Oceanographer*)	5 May 1988	American Samoa
RITS-1989	13 February 1989	Manzanillo, Mexico
(*Discoverer*)	1 March 1989	Easter Is.
SAGA-3 (1990)	13 February 1990	Hilo, HI
(*Akademic Korolev*)	12 March 1990	American Samoa
MAGE-1992	21 February 1992	Los Angeles, CA .
(*Vickers*)	11–12 March 1992	Marquesas Is.
(IGAC-MAGE)	25 March 1992	Los Angeles, CA
RITS-1993	19 April 1993	Papeete, Tahiti
(*Surveyor*)	28 April 1993	20°N, 140°W
RITS-1994	1 December 1993	20°N, 140°W
(*Surveyor*)	13 December 1993	Papeete, Tahiti
ACE-1 (1995)	19 October 1995	Honolulu, HI
(*Discoverer*)	28 October 1995	20°S, 160°W
CSP-1 (1996)	14 March 1996	American Samoa
(*Discoverer*)	17 March 1996	2°S, 180°W
	27–31 March 1996	2°S, 147°E
	8 April 1996	1°S, 180°W
	13 April 1996	Honolulu, HI

PMEL — Pacific Marine Environmental Laboratory marine chemistry cruises

SAGA — Soviet American Gas and Aerosol experiment (1990)

RITS — Radiatively Important Trace Species (1988, 1989, 1992, 1993, 1994)

IGAC-MAGE — International Global Atmospheric Chemistry Program's Marine Aerosol and Gas Exchange Equatorial Pacific Experiment (1992)

ACE — IGAC Aerosol Characterization Experiment (1995)

CSP — Combined Sensor Program (1996)

Zonally and meridionally, the equatorial Pacific Ocean is a region of strong gradients in sea-surface temperature, nutrients, and primary productivity [*Barber and Chavez*, 1991]. These gradients are the result of intense upwelling along the equator which generally increases from west to east. The upwelled nutrients support a biological food web dominated by small phytoplankton [*Chavez et al.*, 1990] and microzooplankton [*Chavez et al.*, 1991]. Grazing by microzooplankton appears to be tightly coupled to primary production rates [*Landry et al.*, 1995], which results in a system that efficiently recycles organic matter in the surface water column. Despite the gradients in SST, nutrients, and primary productivity, this tightly coupled system maintains a relatively constant total biomass across the equatorial Pacific Ocean [*Barber and Chavez*, 1991]. Interestingly, average DMS concentrations, like total biomass, remain relatively uniform from 150°E to 105°W (Figure 3).

Although the lifetime of DMS in surface seawater is about one day [*Kiene and Bates*, 1990; *Bates et al.*, 1994], there is little variation in equatorial Pacific seawater DMS concentrations at a single location over 1– 2 weeks. In 1992, measurements were made along a transect from 15°N to 12°S. A time-series station was held for 7 days at 12°S, 135°W during which seawater DMS concentrations averaged 4.1 ± 0.45 nM (1σ, n = 260) [*Yvon et al.*, 1996; Figure 2h). At the end of the time-series station, the ship returned along the same track. Except for the region near the Marquesas Islands (8°S–10°S), DMS concentrations measured 1–2 weeks later on the northbound leg were identical to those measured on the southbound leg (Figure 2h).

During the past 15 years, ENSO events have occurred in 1982–1983, 1986–1987, and 1990–1995. The PMEL 1983, MAGE 1992, and RITS 1993 cruises occurred during ENSO events. The physical, chemical, and biological oceanographic

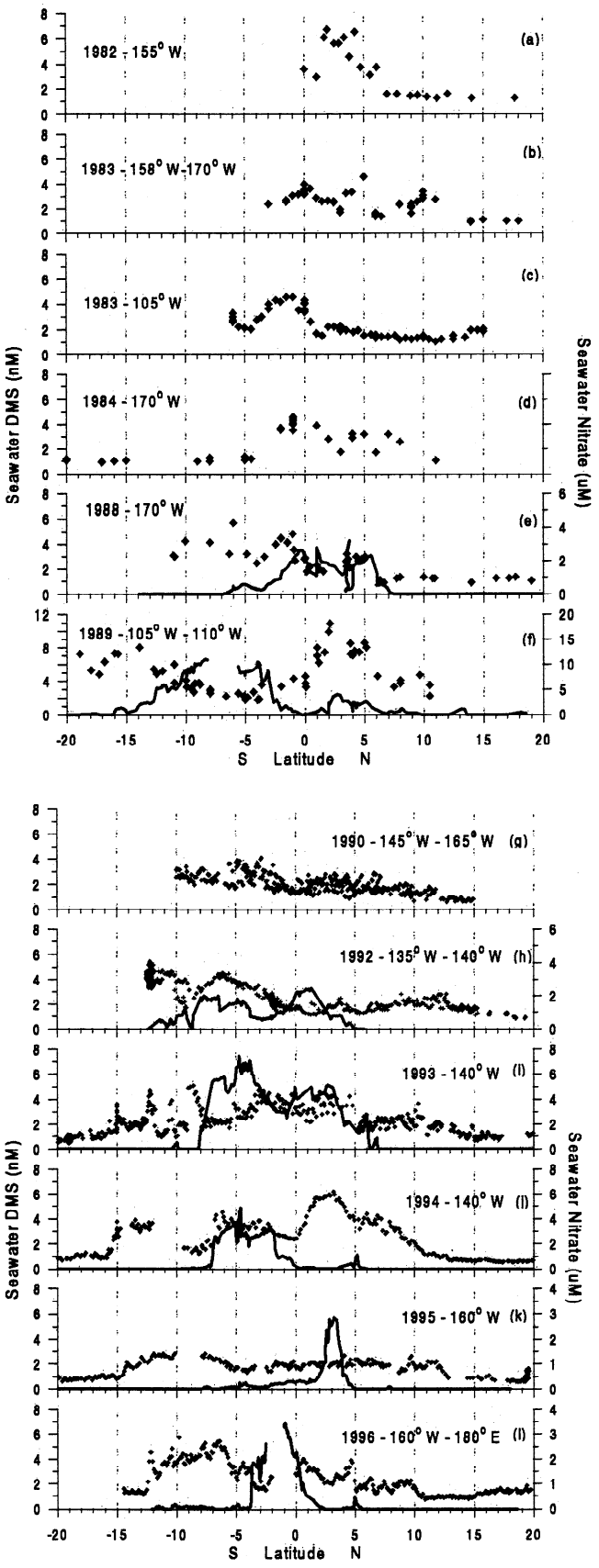

Figure 2. Latitudinal distribution of DMS (◊) in nanomoles/L (nM) and nitrate (line) in micromoles/L (μM) from 20°N to 20°S. The five transects in 1990 were combined and every 5th point was plotted. The DMS distribution in 1992 includes both the southbound (◊) and northbound (+) transects (nitrate southbound only).

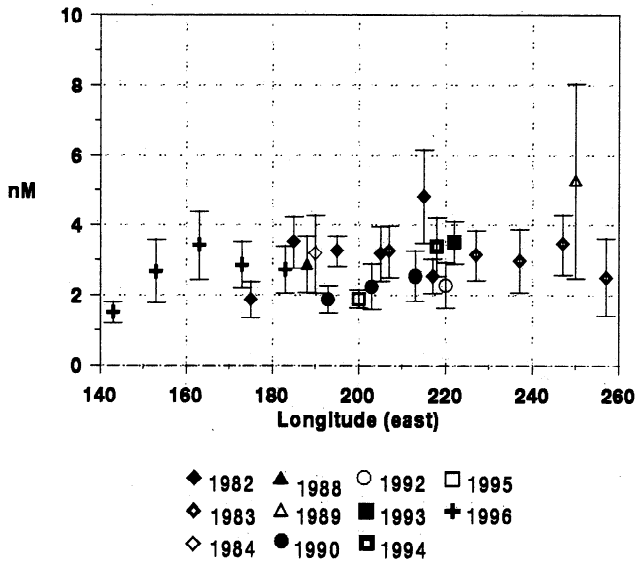

Figure 3. Mean and standard deviation of DMS concentration in 10-degree longitude bins along the equator. The averaged data are from 5°N to 5°S.

features associated with the 1992 ENSO event are the best documented to date [*Murray et al.*, 1994]. Regional cloud fraction nearly doubled with a corresponding reduction in solar insolation, westerly wind anomalies spread across the Pacific, the SEC nearly stopped, the thermocline deepened, and SST rose [*Kessler and McPhaden*, 1995]. Despite these major changes in the physical features of the atmosphere and ocean, the chemical and biological variations were small [*Murray et al.*, 1994]. Surface nitrate concentrations were still sufficient to support the dominant picoplankton community (Figure 2h). Microzooplankton continued to graze at rates close to picoplankton growth rates [*Landry et al.*, 1995]. Although primary productivity decreased during the ENSO event, this decrease appeared to be due to the elimination of the larger plankton species [*Murray et al.*, 1995], especially diatoms, which are not major DMS producers [*Keller and Korjeff-Bellows*, 1996]. One interesting feature in the nutrient distribution during this period was the elevated concentration of seawater ammonia in the region from 1°–12°S [*Murray et al.*, 1995], implying a higher rate of zooplankton grazing. Interestingly, this was also the region of highest DMS concentrations (Figure 2h). The mean seawater DMS concentration between 5°S and 5°N, however, was 2.2 ± 0.8 nM (Figure 4), similar to previous years.

Conclusions

DMS concentrations in the equatorial Pacific Ocean between 15°N and 15°S are enhanced relative to the oceanic gyres. These enhanced concentrations are presumably the result of the dynamic biological community in the equatorial Pacific, which is dominated by picoplankton and microzooplankton grazers. Although the DMS distribution across the equator varied between cruises, there appears to be little interannual, seasonal, or longitudinal variation in mean equatorial seawater DMS concentration during the period 1982–1996. In addition, the large interannual variations in oceanic (SST, mixed layer depths, and upwelling rates) and atmospheric (cloud cover and precipitation) properties associated with ENSO events appear to have little effect on DMS concentrations in surface ocean

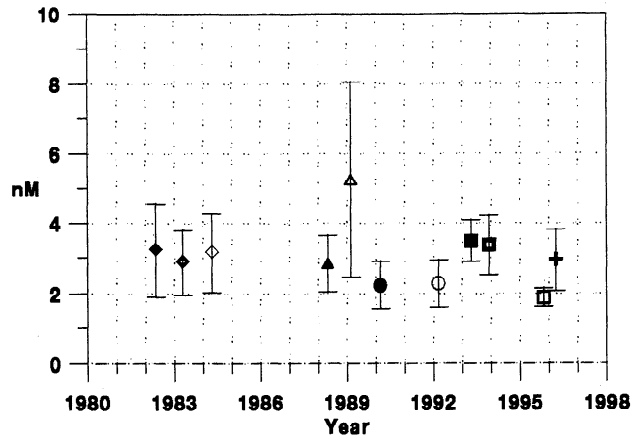

Figure 4. Mean and standard deviation of DMS concentration from 5°N to 5°S for each cruise. The value from 1996 includes the data east of 150°E only.

waters. The hypothesized DMS-climate feedback link thus remains elusive.

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